AD NUMBER

AD817705

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Critical Technology; JUN 1967. Other requests shall be referred to Air Force Rocket Propulsion Lab., Edwards AFB, CA.

AUTHORITY

AFRPL ltr, Jun 1967

DOUBLE-BASE BINDER IMPROVEMENT

Lockheed Propulsion Company
A Division of Lockheed Aircraft Corporation
Redlands, California

TECHNICAL REPORT AFRPL-TR-67-184

June 1967

FOREWORD

This is the first Quarterly Report issued under Contract No. FO4611-67-C-0078, "Double-Base Binder Improvement," covering the period 1 March 1967 through 31 May 1967. This contract is assigned to Lockheed Propulsion Company, Redlands, California and is monitored by Mr. R. C. Corley, Air Force Rocket Propulsion Laboratory, Edwards, California.

Technical effort under this contract has been performed by the following: Dr. W. E. Baumgartner (Program Manager), Dr. G. E. Myers (Principal Technical Investigator), E. E. Larkin, and Waldemar Koehler.

This report is unclassified in its entirety.

Publication of this report does not constitute Air Force approval of the report's findings and conclusions. It is published only for the exchange and stimulation of ideas.

William Ebelke
Colonel, USAF
Chief, Propellant Division

ABSTRACT

An investigation is underway into the physico-chemical factors controlling the mechanical behavior of slurry cast and base grain composite double-base propellants, the primary objective being to improve the mechanical properties of slurry cast systems at least up to those of analogous base grain systems. During this first quarter, efforts were concerned with planning, procurement, and initiation of a program to establish a meaningful physical property comparison between base grain and slurry cast CMDB propellant and among slurry cast propellants containing various types of NC. Further effort was initiation of a task to investigate binder/propellant micro-inhomogeneities using tritium autoradiography.

(The reverse is blank)

TABLE OF CONTENTS

LIST OF TABLES

(The reverse is blank)

SECTION I

INTRODUCTION AND SUMMARY

In this program, an investigation is being conducted into physico-chemical factors controlling the mechanical behavior of slurry cast and base grain composite double-base propellants (CMDB), the primary objective being to improve the mechanical behavior of slurry cast systems to the point where they at least equal those of similar base grain propellants.

The base grain process has been used almost exclusively whenever nitroglycerin serves as a plasticizer and generally (though not always) produces propellants of superior mechanical properties relative to those from the slurry cast process. The latter process, however, possess very distinct processing advantages over the base grain because of its comparative simplicity, safety, and versatility.

While extensive investigations have been made into the general problem of CMDB propellant mechanical behavior, our understanding still remains comparatively poor, in both a fundamental and an applied sense. Considering their wide usage, in fact, nitrocellulose (NC) gels are perhaps the least understood of the major thermoplastic systems. Nevertheless, the CMDB propellants, and particularly those prepared by the slurry cast process, appear at present to offer the greatest potential as a vehicle for high energy ingredients. Thus, a significant improvement in slurry cast propellant mechanical behavior is much to be desired.

Because of the complexity of the CMDB system, any program expecting to achieve significant improvements in mechanical behavior within a reasonable period must be highly selective in its choice of variables for study and in the depth to which it can delve among those variables. In the present program, specific tasks have been selected, each dealing with a critical facet of the overall program. Under each task, the particular phenomena which are believed to be controlling will be singled out for thorough study.

The present report provides an overall summary of the tasks and objectives of the program and a discussion of the first-quarter efforts. The major program tasks are concerned with:

- Detection of various types of binder micro-inhomogeneity, determination of consequent limitations upon physical properties, and study of means to overcome such deficiencies.
- Differentiation among the various factors controlling the separate processes occurring during combined NC solution/gelation/cross-linking to provide the basis for development of an optimized binder system.

- Establishment of the inherent binder-solids adhesional character in the optimized binder system and determination of means to overcome deficiencies to yield an optimized propellant.

First quarter efforts included:

- Necessary planning/procurement
- Initiation of a program to establish a meaningful physical property comparison between base grain and slurry cast CMDB propellants and between slurry cast propellants containing various types of NC.
- Initiation of a task to investigate binder/propellant micro-inhomogeneities using tritium autoradiography.

SECTION II

DISCUSSION

1. GENERAL PROGRAM PLAN

a. Task I - Material Procurement and Analysis

Objectives:

(1) Provide sufficient quantities of well-characterized materials for the entire program, thus eliminating possible contradictory results arising from unrecognized lot variations.

(2) Establish the necessary analytical procedures to, (a) provide a satisfactory definition of material structure/composition and,(b) support fundamental studies conducted under other tasks.

b. Task II - Determination and Correction of Factors Resulting in Binder/Propellant Micro-Inhomogeneity

This task has been subdivided into several subtasks which are related to various types of inhomogeneity known or presumed to exist within DB binders. Some of the more gross examples of these have been positively demonstrated by past investigations. Definitive studies are lacking, however, with regard to the existence of more subtle inhomogeneities, the extent of their influence upon mechanical behavior, and their dependence upon ingredient structure and form. This task sets out first to provide that information, making heavy use of the very sensitive and specific analytical technique, tritium autoradiography, and second, to eliminate deficiencies arising from the inhomogeneities.

Objectives:

Subtask II-1 Overcome deficiencies resulting from incomplete gelation/solution of NC particles caused by NC structural inhomogeneities, e.g., crystallinity, skins, molecular structure.

Subtask II-2 Detect and overcome deficiencies arising from the retention of NC micellar interfaces, i.e., lack of intermicellar diffusion of NC.

Subtask II-3 Detect and overcome deficiencies due to inhomogeneities arising out of processing differences, i.e., the prewetting of solids in the base grain process in contrast to the presumably greater degree of NC diffusion required in the slurry cast process, with probable attendant microregions poor in NC content.

Subtask II-4 Detect and overcome deficiencies resulting from plasticizer/solvent inhomogeneities in formulations containing more than one such liquid.

Subtask II-5 Conduct support efforts to subtasks II-1 to II-4 deemed necessary to elucidate the fundamental processes, e.g., NC swelling and diffusion rates, plasticizer effectiveness, processing variations.

c. Task III - NC Crosslinking

The probability of ultimately attaining the desired mechanical property improvement in CMDB propellants will be considerably enhanced if the physically-structured NC gel can be supplemented by a truly three-dimensional, chemically bonded elastomeric network. Although this fact has long been recognized, the improvements actually achieved have not met the goals desired for these systems, especially if one considers the ballistic sacrifice usually made. This task builds upon the findings of Task II to provide further definition and control of the physical/chemical processes occurring when the complications of the crosslinking reaction are added to the solution/gelation process.

Objectives:

Subtask III-1 Conduct fundamental study of combined crosslink reaction-solution-gelation processes in solids-free binder. It is not now apparent how well separated these processes are either in time or position. The aim here will be to determine the extent of that separation and define the influence of the processes upon resultant physical properties.

Subtask III-2 Extend above (III-1) by determining effects due to solids.

Subtask III-3 Optimize mechanical properties in DB binders and CMDB propellants. The fundamental understanding gained from III-1 and III-2 will be combined here with studies of permissible variations in structure and composition to yield optimized mechanical behavior.

Subtask III-4 Superimpose the requirements of ballistic performance and combustion efficiency upon the above optimized system.

d. Task IV - Binder-Solids Adhesion

Tasks II and III seek an improvement in CMDB propellant mechanical behavior through an optimized binder. The full potential of these systems will never be attained, however, without major enhancement of their notoriously poor binder-solids adhesion.

Objectives:

Subtask IV-1 Determine the basic ability of optimized DB binders to bond various solid surfaces and distinguish between deficiencies arising from that inability and those resulting from limitations within the binder itself (e.g., diffusion phenomena).

Subtask IV-2 Conduct necessary studies to improve binder-solid adhesion, following directions shown by IV-1, e.g., elimination of NC micellar structure and/or use of anti-peel or bonding agents.

e. Task V - Demonstration

Objectives:

(1) Demonstrate propellant mechanical property improvements for slurry cast CMDB propellants using the procedures/compositions identified by the program.

(2) Test the applicability of the above procedures/composition for improving the mechanical properties of base grain CMDB propellant.

2. FIRST QUARTER PROGRAM

Three general objectives were established for the first quarter:

- Perform "service" efforts (Task I) necessary for initiation and conduct of program (e.g., planning, procurement, technique refinement).
- Initiate efforts to obtain physical property data for specific base grain and slurry cast propellant formulations to provide the necessary background information for comparison among the CMDB systems (Task II).
- Initiate studies to determine the presence of various types of inhomogeneity and their relation to physical properties (Task II).

Actual steps taken in pursuit of these objectives are discussed in the following:

a. Propellant Physical Properties

Since the overall aim of the program is to increase slurry cast CMDB propellant behavior to that of base grain, a definitive comparison of presently attainable physical properties is an initial prerequisite. Such a comparison also affords the necessary background information in attempts to correlate differences in behavior with observations upon microstructure (Task II and Section (2) below).

In order to distinguish between plasticizer effects per se and processing differences between slurry cast and base grain systems, two formulations will be employed which are identical except for the use of a "good plasticizer" in Formulation A (Table I) and a "poor plasticizer" in Formulation B. (The terms "good" and "poor" have the usually qualitative connotation in this context of relative ability to produce a homogeneous NC gel.) Ideally, of course, it would be desirable to compare one single "very good' plasticizer versus another single "very poor" plasticizer, but obvious processing and structural integrity limitations necessitate the compromise plasticizer compositions shown in Table I. The casting powder composition for the base grain propellant formulations is given in Table II. It corresponds to Formulation B prepared with a 30/70 casting solvent to casting powder ratio, wherein the casting solvent composition is the same as that in the casting powder.

The program for initial physical property measurements is given in Table III. All testing will be performed at Lockheed Propulsion Company. The base grain propellant samples will be prepared at the Naval Ordnance Station (NOS), while all slurry cast systems will be prepared at LPC. To preclude possible inconsistencies due to ingredient lot variations, single lots of ingredients have been set aside in quantities sufficient for the entire program and are being stored under conditions which will minimize any changes. These lots are being fully characterized. The same lots will also be employed for the base grain propellants prepared at NOS.

b. Presence and Influence of Inhomogeneities

The presence of fairly gross inhomogeneities has been demonstrated in some DB binders by microscopic and/or X-ray radiographic techniques. Because of the similar elemental compositions and structures of NC and plasticizers, however, both of these techniques (as well as electron microscopy) suffer from definite limitations with regard to sensitivity, resolution, and specificity insofar as compositional heterogeneity is concerned. In biological systems, these limitations have been overcome by the application of tritium autoradiographic techniques, which are now very extensively used in that field but whose great potential in other areas has not been widely appreciated.[1]

By virtue of its very low energy, the tritium beta ray has an average path length in organic matter of only about one micron, for example. Thus, compositional inhomogeneity of a tritium-labeled ingredient may be determined with a resolution of about one micron by means of careful radiographic measurements upon thin sections. The relative ease of tritium-labeling in many organic molecules also permits studies upon the distribution of numerous ingredients with essentially complete specificity. Finally, the present autoradiographic films and emulsions are sufficiently sensitive that only small extents of tritium labeling are required and hence structural modifications and radiation-induced degradations are minimal.

---

[1] Evans, E.A., "Tritium and Its Compounds," D. Van Nostrand, New York, 1966

TABLE I

BASIC FORMULATIONS FOR MECHANICAL PROPERTY COMPARISON

Ingredient	Weight Percent A	Weight Percent B
NC	15.0	15.0
TEGDN	14.6	3.4
TMETN	19.4	30.6
AP	25.0	25.0
Al	16.0	16.0
HMX	9.0	9.0
Ethyl centralite	0.5	0.5
Resorcinol	0.5	0.5

TABLE II

CASTING POWDER COMPOSITION FOR FORMULATIONS A & B

Ingredient	Weight Percent
NC	21.46
TEGDN	0.57
TMETN	5.11
AP	35.72
Al	22.86
HMX	12.86
Ethyl centralite	0.71
Resorcinol	0.71

TABLE III

BACKGROUND PHYSICAL TESTING PROGRAM

System	Formulation	Testing
Base Grain	A	Full[1]
	B	Limited[2]
Slurry Cast		
NOS PNC	A	Full
	B	Limited
N92 PNC duPont PNC Ball powder (TMETN impregnated) Ball powder (TMETN impregnated, enzyme treated)	A and B	Limited
Avicell microcrystalline NC	A	Limited

[1] Full testing includes triaxial specimens, biaxial strips, uniaxial tensile (JANAF and miniature) and dewetting studies at temperatures from -40 to + 140°F.

[2] Limited testing includes miniature tensile specimens from -40 to +140°F.

Tritium autoradiography will be employed in this program wherever molecular inhomogeneities and composition gradients are suspected of having a significant influence upon binder/propellant behavior. This applies to the inhomogeneities of NC and plasticizer noted above in Task II, the differentiation among gelation/diffusion/reaction processes occurring during crosslinking (Task III), and effects upon binder-solids adhesion (Task IV). Progress to data in implementing such studies is summarized in the following.

(1) Labeled Ingredients

<u>Nitrocellulose</u> While tritium-labeled materials can be prepared by exposure to tritium gas, significant degradation almost always occurs in this process, necessitating considerable purification. With NC, the resultant product at the very least would be expected to differ greatly from the normal propellant raw material in average molecular weight and distribution and hence, cast doubt upon the significance of subsequent autoradiographic results. Consequently, it has been decided to prepare tritium-labeled NC by reaction of a small number of its residual hydroxyls with a tritium-labeled small molecule. Of the possibilities here, tritiated acetic anhydride has been selected for initial attempts because of its ready availability and the expected ease of accomplishing very small degrees of acetylation.[2] The activity of commercially available tritiated acetic anhydride and the autoradiographic sensitivity are such that less than 1 percent of the residual NC hydroxyls (12.6 percent nitrogen NC) need to be acetylated; this should constitute negligible structural modification of the NC.

The NC sample to be labeled will come from the same fibrous NC lot to be used by NOS in preparing base grain propellant samples and the PNC for this program. The resultant labeled NC will be converted by NOS into small samples of PNC and casting powder for autoradiographic studies at LPC.

<u>Plasticizers</u> Initially, these will be restricted to ethylene glycol dinitrate (EGDN) and trimethylolethane trinitrate (TMETN) as examples of "good" and "poor" plasticizers. Depending upon results with these materials, investigations may be extended to others (NG, TEGDN, etc.)

Tritium-labeled EGDN will be prepared by nitrating commercially available tritiated ethylene glycol, while labeled TMETN will be prepared by nitration of trimethylolethane (TME) synthesized from propionaldehyde and commercially available tritiated formaldehyde in alkaline medium.[3] All steps in these preparations have been carried out using unlabeled ingredients, with no difficulties encountered. Yields of the nitration steps were 95 percent or greater, and that for the TME synthesis was 50 percent.

---

[2] Carrignan, Y. P. and J. Bobinski, Picatinny Arsenal Report No. PA TR-3105 June 1964

[3] Laemmle, Geo. J., et al, Ind. Eng. Chem. <u>52</u>, 33 (1960)

Crosslinker Previous studies at LPC demonstrated that a 1000 molecular weight polyestercaprolactone capped with TDI gave moderate improvements in CMDB mechanical properties--comparable to the improvements reported by Hercules with a polyglycol adipate/TDI. Initial autoradiographic investigation of the combined gelation/diffusion/crosslink reaction processes will, therefore, employ the tritium-labeled polyester-caprolactone/TDI prepared by polymerizing caprolactone with tritiated ehtylene glycol as initiator, followed by capping with TDI.

(2) Autoradiographic Technique

The necessary equipment and materials have been assembled and consultations held with experienced personnel at Brookhaven National Laboratory and Loma Linda University. Preliminary experiments are underway using PNC/TEGDN/tritiated ethylene glycol mixtures to establish the details of techniuqe and requisite tritium activity levels.

SECTION III

FUTURE WORK

Synthetic efforts will continue for the preparation of tritium-labeled materials.

As labeled ingredients are prepared, autoradiographic investigation of microinhomogeneities will be conducted. Data will be correlated with microscopic observations of failure, with physical properties, and with NC form and structure.

Background mechanical property data will be obtained upon base grain and slurry cast propellants.

(The reverse is blank)

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Lockheed Propulsion Company P. O. Box 111 Redlands, California 92373	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

DOUBLE-BASE BINDER IMPROVEMENT

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

First Quarterly Technical Report covering period 1 March through 31 May 1967.

5. AUTHOR(S) (Last name, first name, initial)

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
June 1967	17	0

8a. CONTRACT OR GRANT NO. FO4611-67-C-0078 b. PROJECT NO. 3148 c. BPSN 623148 d.	9a. ORIGINATOR'S REPORT NUMBER(S) LPC Report No. 829-Q-1 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AFRPL-TR-67-184

10. AVAILABILITY/LIMITATION NOTICES

This report is unclassified in its entirety.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Air Force Rocket Propulsion Laboratory Research and Technology Division Air Force Systems Command United States Air Force, Edwards, Calif.

13. ABSTRACT

An investigation is underway into the physico-chemical factors controlling the mechanical behavior of slurry cast and base grain composite double-base propellants, the primary objective being to improve the mechanical properties of slurry cast systems at least up to those of analogous base grain systems. During this first quarter, efforts were concerned with planning, procurement, and initiation of a program to establish a meaningful physical property comparison between base grain and slurry cast CMDB propellant and among slurry cast propellants containing various types of NC. Further effort was initiation of a task to investigate binder/propellant microinhomogeneities using tritium autoradiography.

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Double-base propellants Binder propellant micro-inhomogeneity slurry cast and base grain systems Plasticizers						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through ________________."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through ________________."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through ________________."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.